

# Tuning the Particle Size and Charge Density of the Crosslinked Polystyrene Particles

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**ABSTRACT:** We report the synthesis of charged spherical colloidal particles of poly [styrene-(*co*-2-propene sulfonic acid)] crosslinked with divinylbenzene by emulsion polymerization. The effects of concentration of both the emulsifier and initiator on the polymerization, particle size, and charge density are studied. The particle size is found to be dependent on both the emulsifier and initiator concentration and their power dependencies are different. Below critical micelle concentration (CMC), the particle size varies significantly within a small range of emulsifier concentration. In contrast, particle size decrease is not very pronounced at the heterogeneous (micellar) particle nucleation regime where the emulsifier concentration is well

above of the CMC. The power dependencies of the number of particles on surfactant concentration are explained in the light of conversion–time profile of the polymerization. The surface charge density of the colloidal particles also varies with both the emulsifier and initiator concentration. Both the particle size and charge density show an inverse relation with the molecular weight of the polymer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2718–2725, 2008

**Key words:** colloids; emulsion polymerization; polystyrene; critical micelle concentration (CMC); surface charge density

## INTRODUCTION

For several decades, emulsion polymerization has been widely used for the synthesis of polymeric particles. This polymerization technique is a unique process for the preparation of latex polymer colloids and has several distinct advantages compared to other homogeneous radical chain polymerization.<sup>1,2</sup> Apart from the physical differences, there is one significant kinetic difference between emulsion polymerization and other polymerization processes. Although the other polymerization processes show an inverse relationship between the rate of polymerization and the molecular weight, emulsion polymerization can afford increase in molecular weight without decreasing the rate of polymerization. The mechanism and the kinetics of emulsion polymerization have been reported extensively by several authors; for example, a recent review by Chern<sup>3</sup> has summarized various issues of emulsion polymerization developed so far.

Monodisperse polymer colloidal particles have many applications in various technologies such as paints, coatings, finishes, and floor polishes etc.<sup>1–4</sup>

Among various methods<sup>5–9</sup> employed for the synthesis of monodisperse spherical colloidal particles of polymers such as polystyrene, poly (methyl methacrylate) etc., emulsion polymerization technique is found to be the most reliable one. These monodisperse colloidal particles self-assemble readily at high particle concentration and produce highly ordered close packed colloidal crystals, which exhibit bright iridescence due to Bragg diffraction of light. Also, efforts have been made to prepare highly charged, monodisperse spherical polymer colloidal particles by covalently attaching ionizing groups on the polymer backbone.<sup>10–17</sup> These charged particles are self-assembled in solution in a non close packed three-dimensional array, commonly known as crystalline colloidal array. As atomic crystals diffract X-rays meeting the Bragg condition, colloidal crystalline arrays also diffract ultraviolet, visible, and near-infrared light depending on the lattice spacing.<sup>10–17</sup> These colloidal crystalline arrays have been immobilized into a polymer hydrogel matrix to fabricate sensor materials based on hydrogel volume phase transition.<sup>18,19</sup> In a recent report, it has been demonstrated that colloidal array can also be used to make proton conducting membrane for polymer electrolyte membrane fuel cell.<sup>20</sup>

Since the self-assembly, phase transitions, and the optical properties of these colloidal particle dispersions depend upon the size, charge, size polydispersity, and volume fraction of the particles; it is utmost necessary to control these parameters by altering the emulsion polymerization recipe during the synthesis

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of polymer colloids. There are several factors in the polymerization recipe, such as emulsifier concentration, initiator concentration, monomer concentration, and the reaction temperature, which can alter the particle size and charges.<sup>3,13,14,21,22</sup> Among these, the concentration of the emulsifier and initiator play the major role to optimize the particle size and charges. Emulsifier forms micelles when its concentration exceeds the critical micelle concentration (CMC) and large amount of emulsifier yields large number of smaller sized micelles. During polymerization two types of particle nucleations are possible depending on the amount of emulsifier present in the polymerization mixture. When the emulsifier concentration is around the CMC or well above the CMC, the growth of the particle takes place inside the micelle, known as micellar particle nucleation or heterogeneous particle nucleation. On the other hand, if the emulsifier concentration is well below the CMC, then the particle nucleation takes place on to the emulsifier-stabilized precipitated oligomeric radicals, which is known as homogeneous particle nucleation.<sup>1,23–25</sup> Hence, these two particle nucleation processes can be classified into two regimes as regime-I (below CMC) and regime-II (above CMC). Thorough investigations of various aspects of colloidal particles synthesis by emulsion polymerization in both the regime have been carried out both theoretically and experimentally.<sup>23–29</sup> However, studies on the crosslinked charged copolymer particles are not reported extensively in the literature.<sup>7,13–16,30–32</sup> However, the effect of the emulsifier concentration on the charged crosslinked particle sizes as well as on the particle charges in both regime-I and II have not been studied systematically. This observation prompted us to carry out emulsion polymerization for the synthesis of charged crosslinked colloidal particles by varying the emulsifier concentration in both the regime-I and II. In this article, we are reporting the synthesis and characterization of crosslinked charged spherical polystyrene colloidal particles. We have used sodium salt of 2-propene sulfonic acid (PSA) and sodium dodecyl sulfate (SDS) as the charged monomer and an emulsifier, respectively. Both the charged monomer and emulsifier has been extensively used before and are readily available in the commercial source compared to the others reported in the literature. We have measured the particle size, particle volume fraction, surface charge density, and determined viscosity-average molecular weight of the polystyrene colloidal particles.

## EXPERIMENTAL

### Materials

Styrene (Sisco, India) monomer, divinyl benzene (DVB, Aldrich) crosslinker were purified using the

method described elsewhere<sup>30</sup> to remove the inhibitor. Sodium salt of 2-propene sulfonic acid (PSA) as an ionic comonomer (Polyscience, USA), sodium dodecyl sulfate (SDS) as surfactant (Merck), sodium bicarbonate (Sisco), and ammonium per sulfate (APS, Merck) as the buffer, and an initiator, respectively, were used as received from the suppliers. Dowex mixed bed ion-exchange resin (Sigma-Aldrich) was also used as received. Triple distilled water was used for all experiments.

### Synthesis and purification of colloidal particles

Crosslinked charged polystyrene colloidal particles were synthesized by emulsion polymerization technique in a four-neck mercury-sealed round bottom flask fitted with a reflux condenser, a teflon stirrer attached to a high-torque overhead mechanical stirrer, nitrogen, and reagent inlet. The temperature was maintained by placing the reaction vessel in a controlled temperature oil bath. The reaction vessel was charged with 75 mL of triple distilled water containing 0.1 g of sodium bicarbonate. The water solution was deoxygenated by bubbling nitrogen for 40 min. After thorough deoxygenation, the weighted amount of SDS dissolved in 10 mL of water was added, and the temperature was increased to 50°C. Freshly deoxygenated styrene (33 g, 0.32 mol) and DVB (1.65 g, 0.013 mol) were injected slowly at a constant rate of 4 mL/min. The 2-PSA sodium salt (1.98 g, 0.014 mol) was dissolved in 5 mL of water and injected 10 min after the addition of styrene and DVB. The temperature was increased to 70°C and the stirring speed was increased to 350 rpm. After equilibration for 30 min, required amount of APS dissolved in 10 mL of water was injected into the reaction mixture. The reaction was refluxed for 3–4 h. A nitrogen blanket and the stirring rate of 350 rpm were maintained during refluxing. We have varied both the surfactant (SDS) and initiator (APS) concentration extensively in the reaction mixture and presented in Tables I and II.

A milky white colloidal solution was obtained upon the completion of the reaction. It was then allowed to cool and filtered through glass wool. The filtered solution was centrifuged for 40 min at 45,000 rpm at 15°C in an ultracentrifuge. The residue (solid white mass) was thoroughly dispersed in triple distilled water with the help of sonication and mixing in a vortex motor. Centrifugation and dispersion process were repeated 3–4 times to remove all the impurities from the colloidal polystyrene particles. The particles showed bright iridescence after this purification steps. The colloidal solution was taken in a storage glass bottle and mixed bed ion-exchange resin was added and placed on a vertical rotor for the thorough mixing of the particles with resin.

TABLE I  
Polymerization Recipe and Particle Characterization by Varying Emulsifier Concentration

Sample	SDS (mM)	APS (mM)	Diameter <sup>a</sup> (nm)	PD <sup>b</sup>	Charge Density ( $\mu\text{C}/\text{cm}^2$ )	$N_p$ (no./mL) $\times 10^{-13}$	Measured $\overline{M}_v$
1	0.348	17.54	456	0.32	43.62	0.0559	$2.13 \times 10^4$
2	0.693	17.54	411	0.42	27.70	0.0641	$1.97 \times 10^4$
3	1.734	17.54	229	0.06	14.80	1.23	$36.47 \times 10^4$
4	6.935	17.54	135	0.20	8.16	4.61	$25.83 \times 10^4$
5	13.870	17.54	102	0.17	6.37	9.52	$33.38 \times 10^4$
6	20.806	17.54	88	0.17	4.37	18.48	$38.36 \times 10^4$
7	27.741	17.54	86	0.46	4.19	19.23	$42.60 \times 10^4$
8	69.353	17.54	51	0.13	2.11	43.87	$55.38 \times 10^4$

<sup>a</sup> Diameter measured by Zetasizer.

<sup>b</sup> PD is the polydispersity; obtained from Zetasizer.

### Characterization of colloidal particles

Particle sizes were measured from the dilute solution of colloids using a Zetasizer instrument (Zetasizer 3000HS, Malvern Instruments) at 25°C. The instrument was operating at a wavelength of 633 nm and measurements were carried out at a detection angle of 90°. For each sample at least three measurements were taken to check the repeatability of the results and the analysis was done using CONTIN analysis mode. Particle sizes were also verified from images observed in scanning electron microscope (SEM, Philips-XL30ESEM). Aqueous diluted colloidal juice was dropped on a cleaned glass piece and air dried for SEM experiments. For SEM experiments samples were gold coated and then SEM images were taken.

The polymerization (% of conversion vs. time profile) was followed by removing 2 mL of reaction mixture from the reaction vessel at different time intervals. Hydroquinone (1% by weight) was used to stop the polymerization. The aliquots with 1% hydroquinone at different time intervals were dried in an oven and the percentage of conversion was measured gravimetrically. Particle volume fractions were measured gravimetrically in triplicate considering the polystyrene density as 1.05 g/cm<sup>3</sup>.<sup>33</sup> Particle charge densities were measured by potentiometric titration.<sup>34</sup> Since the crosslinked polymer can not be dissolved fully in any solvent, crosslinker free linear polystyrene samples were prepared separately using

the similar recipe mentioned in Tables I and II for the molecular weight measurements. All these crosslinker free samples were purified in a similar way as aforementioned for crosslinked particles. The viscosity of the freeze-dried samples was measured in butan-2-one solvent using Cannon Ubbelohde dilution viscometer at 30°C. The viscosity-average molecular weight ( $\overline{M}_v$ ) of the samples were determined using the Mark-Houwink relation,  $\eta = K\overline{M}_v^a$ ; where values of  $K$  is  $3.9 \times 10^{-4}$  and " $a$ " is 0.58, respectively, for polystyrene in buta-2-one at 30°C.<sup>35</sup>

## RESULTS AND DISCUSSION

### Particle size versus emulsifier concentration

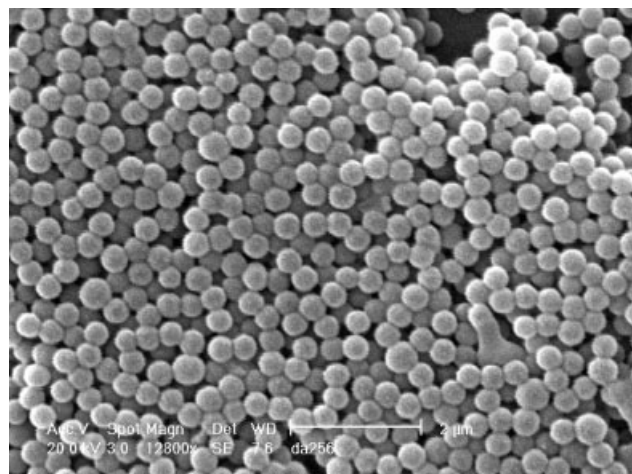
Charged, crosslinked styrene-DVB-2-PSA copolymer colloidal particles with diameter 51–456 nm were synthesized by varying emulsifier concentration in both regime-I (below CMC) and II (above CMC). The detail reaction recipes, particles, and polymers characterizations are listed in Table I. In all the cases monomers, crosslinker, and initiator concentrations are kept constant. Also, the reaction conditions such as temperature, stirring speed, and reflux time etc. for all the reactions are same. The only parameter that we have varied in these reactions is the emulsifier concentration. The CMC of SDS emulsifier is 8.1 mM. This CMC value of SDS has been well established and reported in the literature by several

TABLE II  
Polymerization Recipe and Particle Characterization by Varying Initiator Concentration

Sample	SDS (mM)	APS (mM)	Diameter <sup>a</sup> (nm)	PD <sup>b</sup>	Charge Density ( $\mu\text{C}/\text{cm}^2$ )	$N_p$ (no./mL) $\times 10^{-13}$	Measured $\overline{M}_v$
9	13.87	8.77	99	0.20	3.069	18.36	$31.07 \times 10^4$
5	13.87	17.54	102	0.17	6.374	9.52	$33.38 \times 10^4$
10	13.87	26.31	101	0.07	4.492	10.10	$21.95 \times 10^4$
11	13.87	35.08	107	0.15	7.364	6.59	$18.0 \times 10^4$
12	13.87	43.86	108	0.17	5.752	10.43	$19.68 \times 10^4$

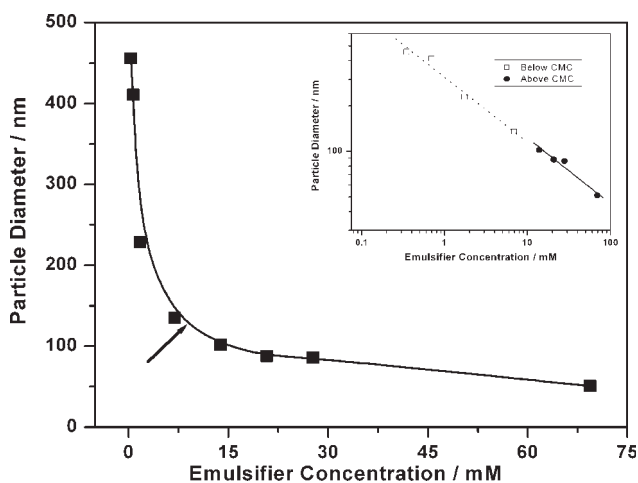
<sup>a</sup> Diameter measured by Zetasizer.

<sup>b</sup> PD is the polydispersity; obtained from Zetasizer.

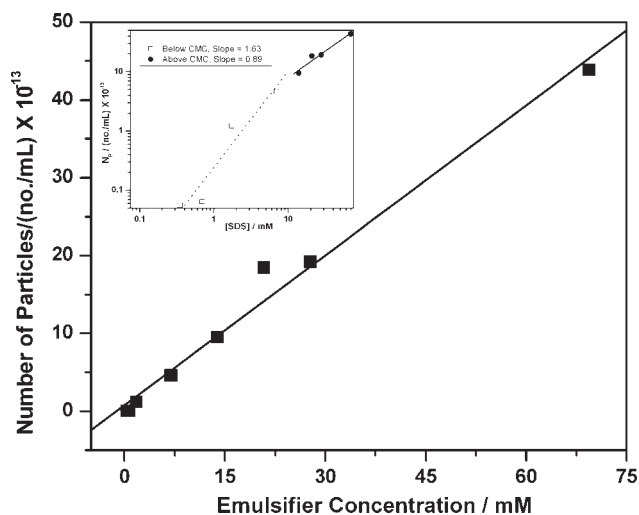


**Figure 1** SEM image of colloidal spheres obtained from Sample-2 in Table I; particle size is 404 nm.

authors. We have used the emulsifier concentration as low as 0.348 mM (sample-1) and as high as 69.35 mM (sample-8) in the polymerization. Figure 1 shows a representative SEM micrograph of the colloidal spheres of 404 nm sizes obtained from sample-2. All the particles are spherical in shape as evident from the SEM image. Particle sizes measured by the Zetasizer for all the samples are listed in Table I. We have observed a very little variation (less than 10%) between particle sizes measured by Zetasizer and microscopy. Particle sizes obtained from Zetasizer are little bigger because it measures the hydrodynamic size of the particles whereas microscopic technique gives the size of dry particles.<sup>14</sup> The variation of particle diameter with increasing emulsifier concentration is plotted in Figure 2. The arrow in the figure indicates the CMC of the emulsifier. The diameter decreases as



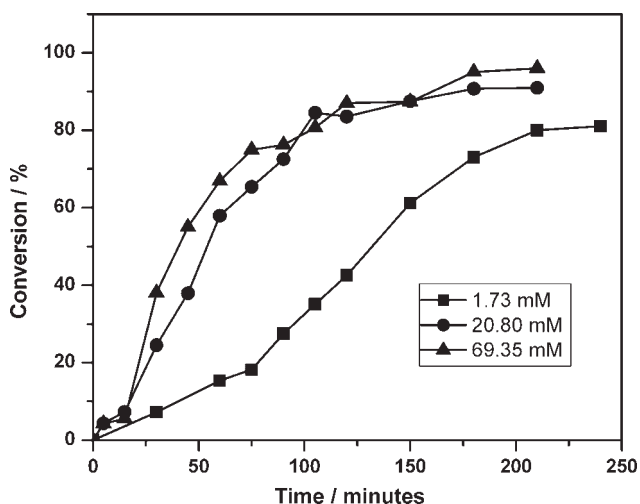
**Figure 2** Effect of emulsifier concentration ( $S$ ) on particle size ( $D$ ) at a fixed initiator concentration; arrow indicates CMC of the emulsifier. Inset: A double logarithmic plot of  $D$  versus  $S$ .



**Figure 3** Plot of number of particles versus emulsifier concentration at a fixed initiator concentration.

the surfactant concentration increases since the lower surfactant concentration produces less number of micelles resulting in bigger particles.<sup>1,13,21,22,36</sup> Figure 3 demonstrates that the number of particles ( $N_p$ ) follows a linear relationship with the surfactant concentration which results an inverse relationship of  $N_p$  with particle diameters.<sup>13,21,22,37</sup>

A careful analysis of Figure 2 reveals that the particle size is decreasing very sharply with increasing emulsifier concentration below the CMC (regime-1) whereas the decrease in particle size is not very prominent with the change of surfactant concentration after the CMC (regime-II). Therefore, a larger tuning of particle size can be achieved within the small range of concentration in regime-I compared to regime-II, though the particle size ( $D$ ) dependence on the surfactant concentration ( $S$ ) in both the regime is  $D \propto S^{-0.43}$ , which is obtained from the slopes of the double logarithmic plot of  $D$  against  $S$  (Inset of the Fig. 2). The dependence of the number of particles ( $N_p$ ) with the surfactant concentration ( $S$ ) in both the regimes is obtained from the log-log plot of  $N_p$  against  $S$  and presented in the inset of the Figure 3. It shows that  $N_p \propto S^{1.63}$  in regime-I and  $N_p \propto S^{0.89}$  in regime-II. The positive exponent of  $N_p \propto S$  is in agreement with the basic principle of emulsion polymerization<sup>21,29</sup> and indicates that the rate of polymerization will be higher for higher surfactant concentration which is clearly visible in the conversion-time profile presented in the Figure 4. The exponent values of  $N_p \propto S$  obtained here are similar to the reported values,<sup>1,21,29</sup> and reveal that in the both the cases coagulative nucleation process takes place. However, different exponent values obtained from the inset of Figure 3 for two regimes indicate that the particle growth mechanisms in regime-I and regime-II are not exactly similar. A critical analysis of the conver-



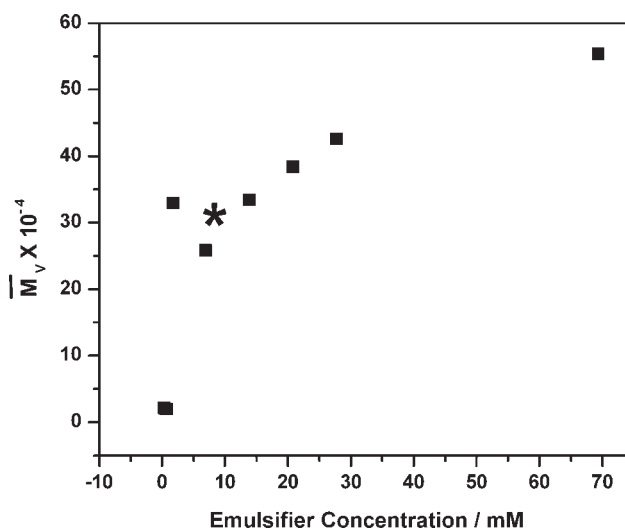
**Figure 4** Conversion versus time profile at the indicated emulsifier concentration.

sion-time profile (Fig. 4) demonstrates that the polymerization rates are quite different in regime-I compared to regime-II. When the emulsifier concentration is below the CMC, conversion increases slowly whereas it increases rapidly above the CMC. Also, we have observed that the yield of the polymerization is much higher in the regime-II than regime-I. These observations clarify that the particle growth mechanisms are different for below and above the CMC. When the emulsifier concentration is well below of its CMC as in regime-I, it does not form any micelle. Therefore, polymerization starts in the aqueous medium itself and water insoluble oligomeric radicals produced are precipitating out from the aqueous medium. These oligomeric radicals become stabilized by absorbing surfactant and further particle growth proceeds on to these oligomeric radicals.<sup>38</sup> In regime-II, particle nucleation occurs inside the micellar core. In case of emulsion polymerization, the rate of polymerization and molecular weight of the polymer can be increased by increasing emulsifier concentration at constant initiation rate, that is, by keeping initiator concentration unchanged. In regime-I, the evolution of viscosity-average molecular weight ( $\bar{M}_v$ ) with emulsifier concentration is more compared to regime-II as evident from the Figure 5. It is clear from Figure 5 that the  $\bar{M}_v$  increases very sharply up to the CMC of emulsifier (as asterisk indicates in the Fig. 5) and then it levels up gradually. Therefore, it can be argued that molecular weight of the polymer and polymerization rate play an important role for the variation of particle diameter with emulsifier concentration in both the regimes-I and II. We have cross checked the particle size of the crosslinker free samples with crosslinked particles. The size differences are less than 10% in most of the cases. Hence, the viscosity-average molecular weights obtained from

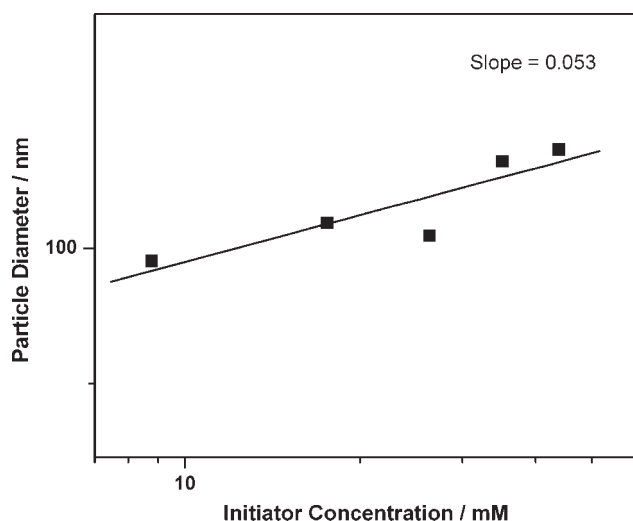
crosslinker free sample can be utilized for cross-linked particles for comparisons.

#### Particle size versus initiator concentration

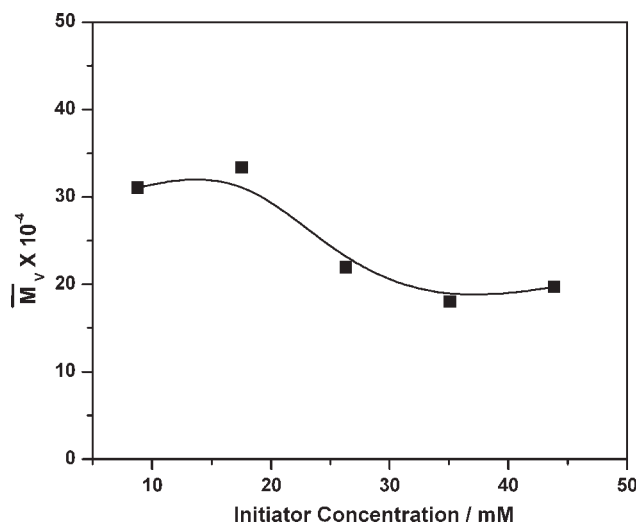
A series of charged spherical crosslinked colloidal particles of diameter varying from 99 to 108 nm have been synthesized by changing the initiator concentration in the emulsion polymerizations recipe. All other parameters for these reactions are kept constant. Polymerization recipe, particle, and polymer characterization are presented in Table II. It is to be noted that the concentration of emulsifier used for all these polymerization is 13.87 mM, which is above the CMC of the emulsifier. Therefore, all these polymerizations belong to regime-II and follow the micellar particle nucleation. A plot of the particle size against the initiator concentration is shown in Figure 6 (log-log plot). The particle diameter increases with increasing initiator concentration linearly; although the increase in size is very small over the initiator concentration (I) range studied here. The dependence exponent is only 0.053 i.e.,  $D \propto I^{0.053}$ , is very low compare to the emulsifier dependence exponent (0.43) aforementioned. A probable reason for this is that at a fixed surfactant concentration the rates of the reactions are not very much different for the different initiator concentrations in regime-II. The conversation-time profile presented in Figure 7 clearly demonstrates that up to  $\sim 50\%$  conversions, the rates are independent of initiator concentration. Therefore, from the above observations we may conclude that in the regime-II, the initiator concentration does not affect the particle size and the rate significantly. This observation is not matching with the earlier



**Figure 5** Plot of  $\bar{M}_v$  versus emulsifier concentration at a fixed initiator concentration.



**Figure 6** Effect of initiator concentration on particle size at a fixed emulsifier concentration.



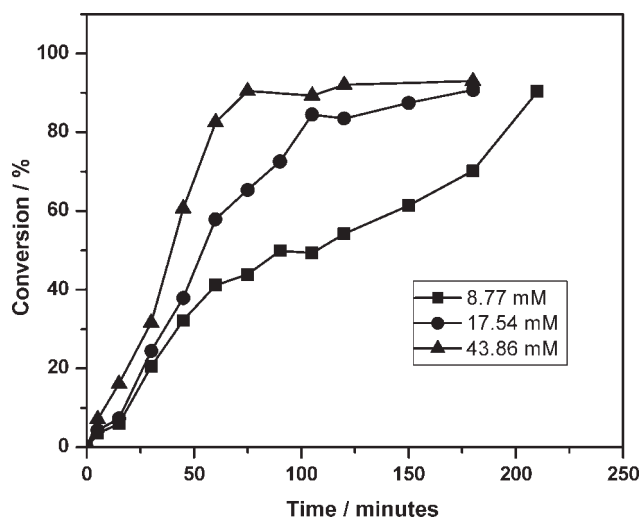
**Figure 8** Plot of  $\bar{M}_v$  versus initiator concentration at a fixed emulsifier concentration.

observation reported in the literature for linear polystyrene. Since the particles studied here are crosslinked charged polystyrene; hence, it may not be worthy to compare this observation with the reported ones. A thorough understanding of the crosslinker effects on the charged particles is under progress. The number of particles<sup>37</sup> as well as the molecular weights<sup>9</sup> maintains an inverse relationship with the initiator concentration for a fixed surfactant concentration (above CMC) as presented in Table II and Figure 8, respectively. It is well known that the polymer molecular weight decreases as the initiator concentration increases. It has also to be noted that, an inverse correlation between the particle size and the molecular weight (the larger particles have the lowest molecular weight) is

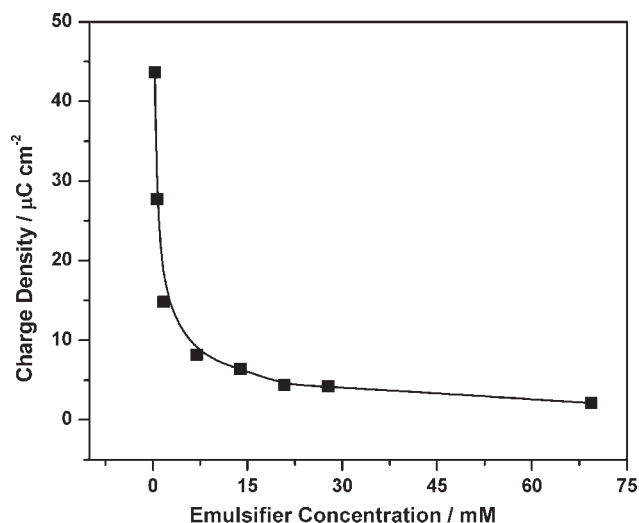
observed for both emulsifier and initiator concentration variation. Similar observation was noted in case of polystyrene particles prepared by the dispersion polymerization.<sup>9,39</sup>

#### Surface charge density of the colloidal particles

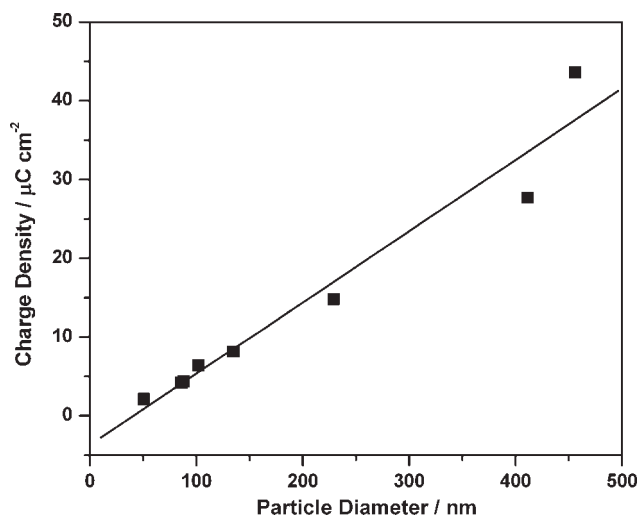
The influences of emulsifier and initiator on particle surface charge density have been studied by varying the concentration of SDS and APS, respectively, in the emulsion polymerization recipes. Figure 9 shows that the charge density decreases as the emulsifier concentration increases. This inverse correlation between the charge density and the emulsifier con-



**Figure 7** Conversion versus time profile at the indicated initiator concentration.



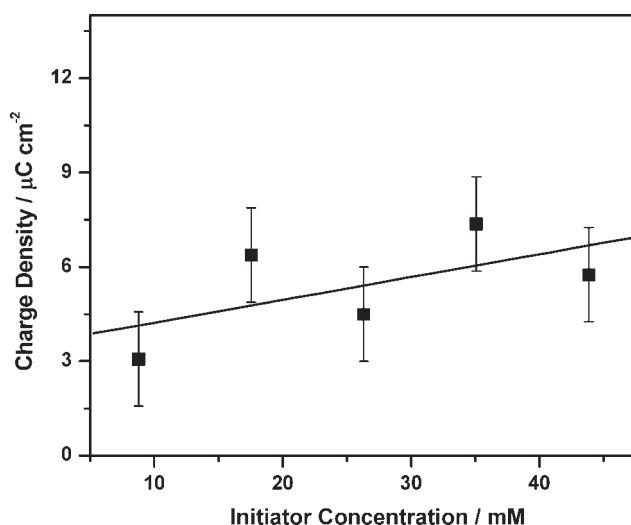
**Figure 9** Charge density versus SDS concentration at a fixed APS concentration.



**Figure 10** Charge density versus particle diameter at a fixed APS concentration.

centration is quite obvious since the charge density is directly proportional to the particle diameter<sup>40</sup> (Fig. 10) and inversely proportional to the molecular weight.<sup>16</sup> Figure 10 shows increase of charge density as a function of particle diameter.

A plot of charge density against the initiator concentration is presented in Figure 11. The line in the figure is the best fit line. Although the deviation of the data points from the best fit line is a bit higher, yet it is clear from Figure 11 that the surface charge density increases as the initiator concentration increases. This observation is in good agreement with the previous report in the literature.<sup>16</sup> Asher and coworkers<sup>16</sup> showed that the charge density and molecular weight is inversely proportional. Since the molecular weight is decreasing with increasing initiator concentration (Fig. 8 and Table II), therefore, it



**Figure 11** Charge density versus APS concentration at a fixed SDS concentration.

is expected that surface charge density will increase with increasing initiator concentration. However, the charge density variation in Figure 11 is low compared to Figure 9, which indicates that the optimization of particle surface charge can be achieved more reliably by varying emulsifier concentration than the initiator concentration.

## CONCLUSIONS

A series of charged crosslinked spherical polystyrene particles of different sizes have been synthesized by emulsion polymerization and characterized. The amount of emulsifier in the polymerization recipe was varied both in below the CMC region (regime-I) and above the CMC region (regime-II). The decrease in particles size with increasing emulsifier concentration in two regimes is not similar; it is more visible in the regime-I compare to regime-II. In contrast to the inverse relationship of the particle size with the emulsifier concentration, there is a direct proportional correlation of the particle size with the initiator concentration. The exponent for particle size dependence in case of emulsifier variation is bigger ( $-0.43$ ) compared to initiator variation ( $0.053$ ), which implies that the variation of the emulsifier concentration would be the better way to prepare particles of different sizes. The dependence of the number of particles with surfactant concentration in both the regime is different and probably this is because the polymerization rates are different in two regimes. The measured molecular weight increases with increasing emulsifier concentration and decreases with increasing initiator concentration. Particle size and molecular weight is inversely related, that is, higher molecular weight produces smaller particle and vice versa. The surface charge density of the particles also depends upon the emulsifier concentration and the initiator concentration. However, the optimization of the charge density of the colloidal particles can be done more efficiently by varying the emulsifier concentration rather than the initiator concentration.

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